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Reactions of an Azidoborane with Phosphines: Synthesis of N-Boryliminophosphoranes

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Abstract

A series of N-boryliminophosphoranes (compounds containing the B-N=P linkage) have been prepared by the reactions of a sterically hindered azidoborane, $(\text{Me}_3\text{Si})_2\text{NB}(\text{tBu})\text{N}_3$ (1), with some three- and two-coordinate phosphines. Treatment of the (silylamino)phosphines $(\text{Me}_3\text{Si})_2\text{NP}(\text{R})\text{Me}$ and the simple aminophosphine $(\text{Me}_2\text{N})_2\text{PPh}$ with 1 gave the corresponding four-coordinate N-boryliminophosphoranes, $(\text{Me}_3\text{Si})_2\text{NP}(\text{R})(\text{Me})=\text{NB}(\text{tBu})\text{N}(\text{SiMe}_3)_2$ (2: R = Ph; 3: R = Me) and $(\text{Me}_2\text{N})_2\text{P}(\text{Ph})=\text{NB}(\text{tBu})\text{N}(\text{SiMe}_3)_2$ (4). Similarly, the reactions of 1 with the two-coordinate phosphorus species, $(\text{Me}_3\text{Si})_2\text{NP}=\text{ESiMe}_3$ (E = CH, N), afforded the first N-borylimino derivatives of three-coordinate, pentavalent phosphorus, $(\text{Me}_3\text{Si})_2\text{NP}(=\text{ESiMe}_3)=\text{NB}(\text{tBu})\text{N}(\text{SiMe}_3)_2$ (5: E = CH; 6: E = N). Compounds 2 - 6 were characterized by NMR (^1H , ^{13}C , ^{31}P , and ^{11}B) spectroscopy and elemental analysis. (M J N)

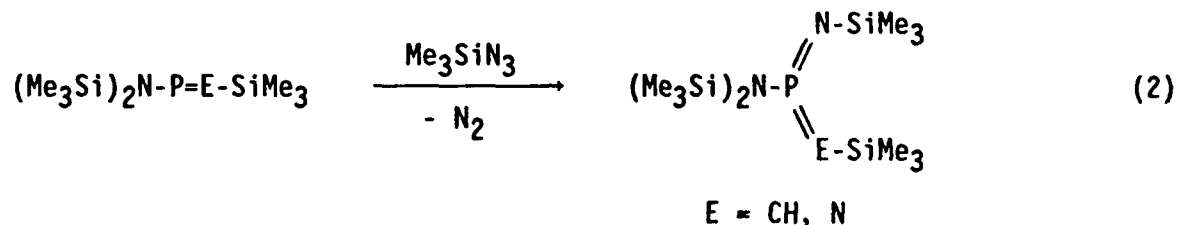
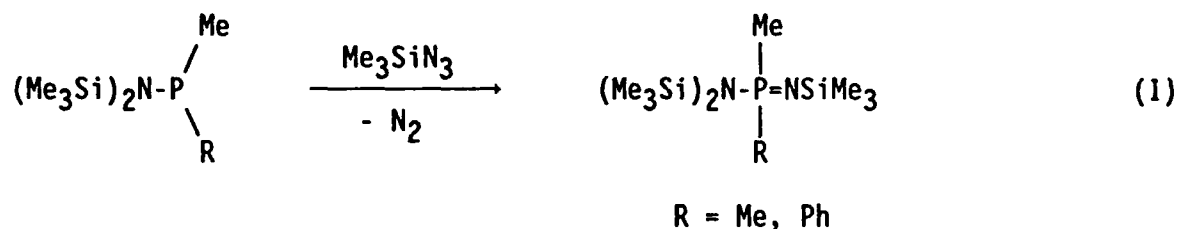


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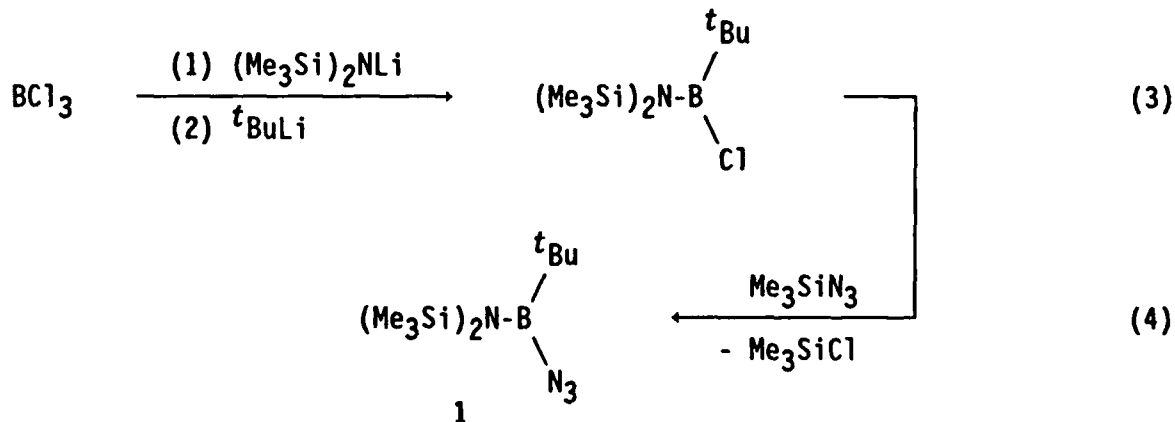
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Introduction

The oxidation of organophosphines with covalent azides, the well-known Staudinger reaction,^{1,2} is a very useful method for preparing the pentavalent iminophosphorane derivatives ($R_3P=NR$). The high thermal stability and ready availability of silyl azides³ makes this method particularly useful for the synthesis of *N*-silylphosphoranimines such as those derived from either the (silylamino)phosphines (eq 1)⁴ or the two-coordinate methylene⁵ and iminophosphines⁶ (eq 2).



Much of our recent work has involved the preparative chemistry of new Si-N-P,⁷ Si-N-B,^{8,9} and B-N-P¹⁰ compounds as possible precursors to and/or model systems for new inorganic polymers. For example, we have reported the synthesis of the stable azidoborane **1** (eqs 3 and 4) by a straightforward route starting from BCl_3 .

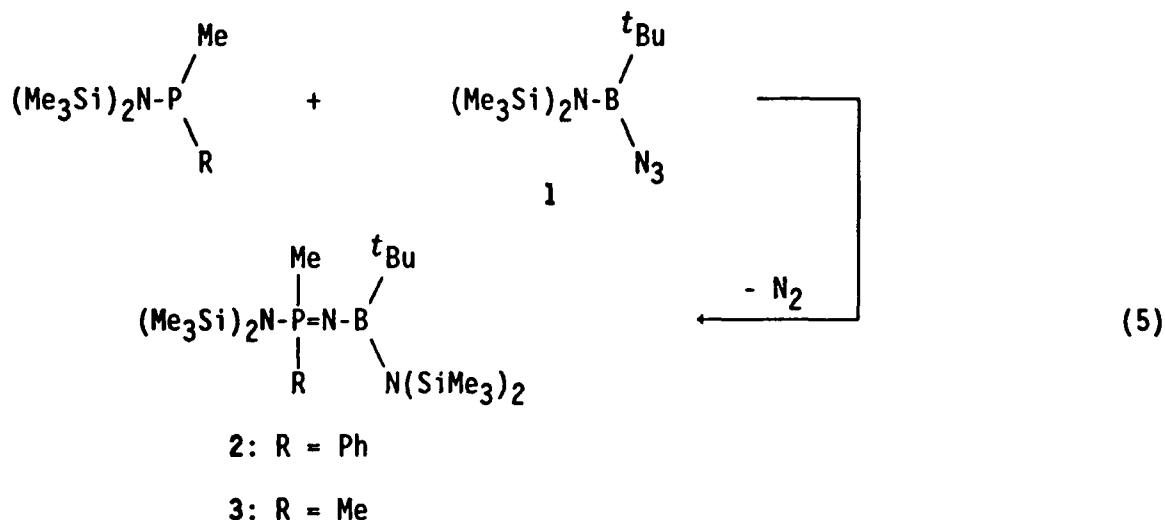


As a continuation of these earlier studies, and in an effort to develop new synthetic routes to B-N-P compounds,¹¹ we report here a series of reactions of the azidoborane **1** with some representative aminophosphines of both the two- and three-coordinate variety.

Results and Discussion

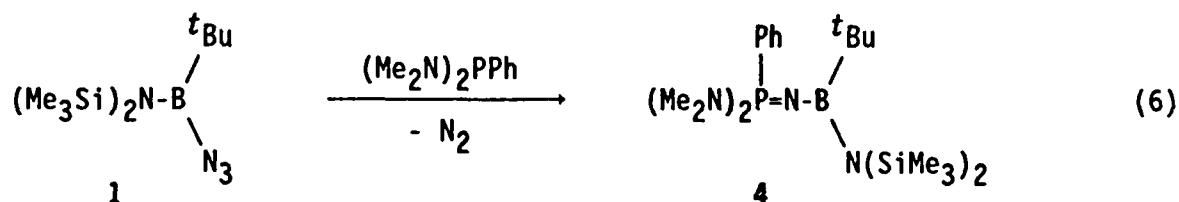
The azidoborane **1** was selected for this study because (1) it is easily prepared (eqs 3 and 4) and isolated in high purity, (2) it is thermally stable to distillation and can be conveniently stored as a solution in hexane, and (3) its sterically bulky substituents should help to stabilize the products of its reactions with low-coordinate phosphorus species.

The oxidation of (silylamino)phosphines with **1** (eq 5) occurred smoothly in hexane solution at ca. 50-65°C. The reactions were easily monitored by ³¹P NMR spectroscopy which indicated quantitative conversion to the N-boryliminophosphoranes **2** and **3** over a period of several hours. The P-phenyl derivative **2** (a white solid) was obtained in 65-70% yields, whereas the P-methyl analogue **3** (a colorless liquid) always underwent significant thermal decomposition during distillation. This reduced the distilled yields of **3** to 20-30%, although the crude product was essentially pure (based on NMR spectroscopy). Although the exact decomposition pathway is uncertain, the ³¹P NMR spectral data indicate that one of the decomposition products is the *N*-silylphosphoranimine, (Me₃Si)₂NPMe₂=NSiMe₃.⁴



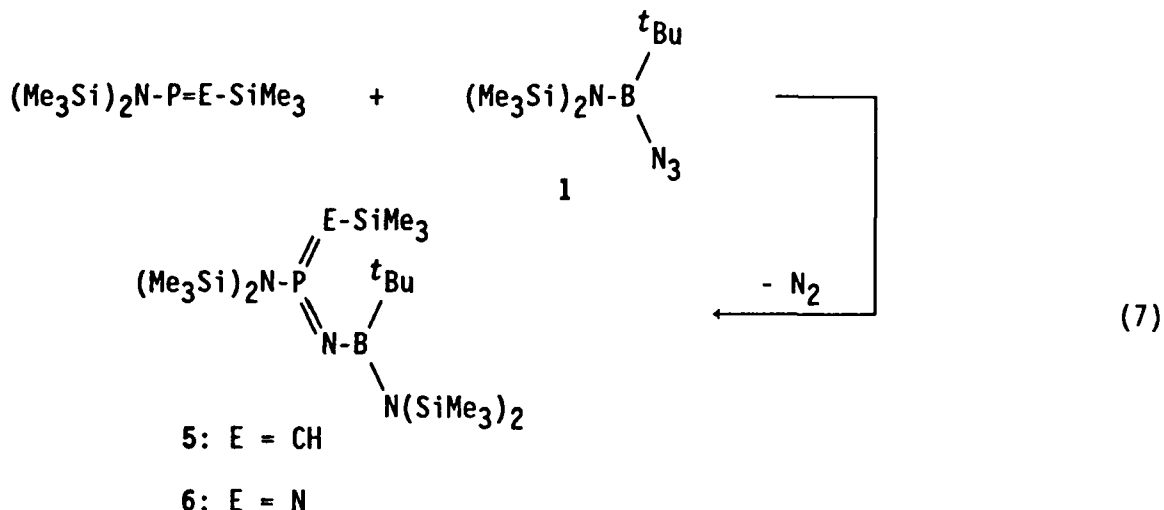
The N-boryliminophosphoranes **2** and **3** were readily characterized by NMR spectroscopy (Table I) and elemental analyses (Table II). Both the ^1H and ^{13}C NMR spectra contain two distinct resonances for the $(\text{Me}_3\text{Si})_2\text{N}$ substituents attached to boron and phosphorus, in addition to the expected ^tBu , P-Me, and phenyl signals. The large $^1J_{\text{PC}}$ and $^2J_{\text{PH}}$ values observed for the P-Me groups are particularly diagnostic of the P^{V} oxidation state in Si-N-P compounds.⁴ The ^{31}P chemical shifts, which are upfield relative to those of the starting phosphines, are also indicative of an oxidized product, while the low-field ^{11}B NMR signals (ca. δ 40-43) are consistent with a three-coordinate boron environment.

In addition to the reactions of the azidoborane **1** with (silylamino)phosphines, we also conducted a series of small scale, "NMR tube" experiments involving the dimethylaminophosphines, $(\text{Me}_2\text{N})_n\text{PPh}_{3-n}$ ($n = 1, 2, 3$). In each case, the reaction was found to be complete under conditions similar to those described above. A typical example (eq 6) was then carried out on a preparative scale and the N-boryliminophosphorane **4** was isolated in 71% yield as a distillable liquid that solidified upon standing.



The oxidation of phosphines by the azidoborane **1** is not limited to simple three-coordinate P^{III} centers. Indeed, we found that the two-coordinate methylene- and iminophosphines were both readily oxidized by **1** to give the novel three-coordinate P^{V} derivatives **5** and **6** (eq 7). Compounds **5** and **6** are both thermally stable products that were isolated in good yields by distillation (**5**) or recrystallization (**6**) and fully characterized by NMR spectroscopy (Table I), elemental analyses (Table II), and mass spectroscopy. The mass spectra of both compounds contained small (ca. 1% relative intensity) molecular ion peaks, large $\text{M}^+ - \text{CH}_3$ (ca. 30%) peaks, and base peaks corresponding to $\text{M}^+ - ^t\text{Bu}$. Interestingly, the ^{31}P NMR chemical shifts of **5** (δ 56.3) and **6** (δ 3.5) occur ca. 50 ppm upfield relative to their N-SiMe₃ analogues, $(\text{Me}_3\text{Si})_2\text{NP}(=\text{ESiMe}_3)=\text{NSiMe}_3$ [$\text{E} = \text{CH}$ (δ 103)⁵; $\text{E} = \text{N}$ (δ 55)⁶]. The reason for such unusually high field chemical shifts is not readily apparent, but they are probably due to increased shielding of the phosphorus by the sterically bulky $-\text{B}(^t\text{Bu})\text{N}(\text{SiMe}_3)_2$ substituent on the

P=N nitrogen. Various trends in the ^{31}P shifts of other three-coordinate phosphoranes have been summarized recently.¹²



In summary, this work has demonstrated that the azidoborane **1** is a useful reagent for the oxidation of both two- and three-coordinate phosphines to afford new N-boryliminophosphoranes. These results suggest that similar phosphorus derivative chemistry of other, less hindered, azidoboranes should be explored.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: PhPCl_2 , Me_3SiN_3 , and $\text{Me}_3\text{SiNMe}_2$. Hexane and ether were distilled from CaH_2 prior to use. Bis(dimethylamino)(phenyl)phosphine, $(\text{Me}_2\text{N})_2\text{PPh}$,¹³ was prepared by the addition of two molar equivalents of $\text{Me}_3\text{SiNMe}_2$ to PhPCl_2 in ether at 0°C . The (silylamino)phosphines, $(\text{Me}_3\text{Si})_2\text{NP(R)Me}$ ($\text{R} = \text{Ph, Me}$)¹⁴ and $(\text{Me}_3\text{Si})_2\text{NP}=\text{ESiMe}_3$ ($\text{E} = \text{CH}^{5\text{a}}, \text{N}^{15}$) were prepared and purified according to the published procedures. The azidoborane, $(\text{Me}_3\text{Si})_2\text{NB}^t\text{(Bu)N}_3$ (**1**), was prepared by the reaction of Me_3SiN_3 with the chloroborane $(\text{Me}_3\text{Si})_2\text{NB}^t\text{(Bu)Cl}$ as previously reported.¹⁰ After removal of the excess silyl azide, undistilled **1** was checked for purity by ^1H and ^{13}C NMR spectroscopy and then dissolved in dry hexane to give a 2.0 M stock solution of **1** for use in subsequent reactions. Proton, $^{13}\text{C}\{^1\text{H}\}$, and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were recorded on a

Varian XL-300 spectrometer; $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained on a JEOL FX-60 Instrument. Mass spectra were obtained on a Finnigan GC-MS Instrument. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The following procedures are representative of those used for the synthesis of the new compounds prepared in this study.

Preparation of $(\text{Me}_3\text{Si})_2\text{NP}(\text{Ph})(\text{Me})=\text{NB}^t(\text{Bu})\text{N}(\text{SiMe}_3)_2$ (2). The aminophosphine $(\text{Me}_3\text{Si})_2\text{NP}(\text{Ph})\text{Me}$ (11.3 g, 40 mmol) was added via syringe to a stirred solution of the azidoborane **1** (20 mL, 2.0 M, 40 mmol) in hexane. The mixture was then refluxed (at ca. 65°C) overnight. The mixture was cooled to room temperature and the solvent was removed under reduced pressure leaving **2** as a white solid that was purified by recrystallization from hexane or CH_2Cl_2 . (Tables I and II)

Preparation of $(\text{Me}_3\text{Si})_2\text{NPMe}_2=\text{NB}^t(\text{Bu})\text{N}(\text{SiMe}_3)_2$ (3). In a similar manner, **1** (18 mL, 2.0 M, 36 mmol) was treated with $(\text{Me}_3\text{Si})_2\text{NPMe}_2$ (8.0 g, 36 mmol) in hexane and the mixture was heated at 50°C for 3 hours. After solvent removal, the viscous liquid residue was identified by NMR spectroscopy as **3** with only minor impurities being noted. Fractional distillation resulted in partial thermal decomposition [to $(\text{Me}_3\text{Si})_2\text{NPMe}_2=\text{NSiMe}_3^4$ and other unidentified products], but a pure fraction (3.4 g) of **3** was isolated.

Preparation of $(\text{Me}_2\text{N})_2\text{P}(\text{Ph})=\text{NB}^t(\text{Bu})\text{N}(\text{SiMe}_3)_2$ (4). Similarly, the aminophosphine, $(\text{Me}_2\text{N})_2\text{PPh}$ (3.9 g, 20 mmol) was added to a hexane solution of **1** (10 mL, 2.0 M, 20 mmol) and the mixture was refluxed for 4 hours. Solvent removal, followed by distillation gave **4** (6.2 g) as a colorless liquid that crystallized on standing at room temperature.

Preparation of $(\text{Me}_3\text{Si})_2\text{NP}(=\text{CHSiMe}_3)=\text{NB}^t(\text{Bu})\text{N}(\text{SiMe}_3)_2$ (5). Similarly, the (methylene)phosphine, $(\text{Me}_3\text{Si})_2\text{NP}=\text{CHSiMe}_3$ (9.7 g, 35 mmol) was added to a hexane solution of **1** (36 mmol) and the mixture was stirred at room temperature for 3 days. Solvent removal, followed by distillation, afforded **5** (18.2 g) as colorless liquid.

Preparation of $(\text{Me}_3\text{Si})_2\text{NP}(=\text{NSiMe}_3)=\text{NB}^t(\text{Bu})\text{N}(\text{SiMe}_3)_2$ (6). The iminophosphine, $(\text{Me}_3\text{Si})_2\text{NP}=\text{NSiMe}_3$ (15.5 g, 56 mmol) was added to a neat sample of **1** (15.1 g) (preliminary experiments showed that this reaction was very slow in hexane solution) and the mixture was heated overnight at ca. 95°C . At

this point, the mixture had turned to a white solid from which pure **6** (20.9 g) was obtained by recrystallization from CH_2Cl_2 .

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References and Notes

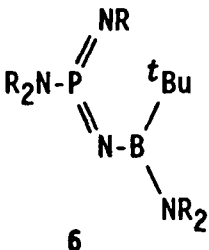
1. Abel, E. W.; Mucklejohn, S. A. *Phosphorus and Sulfur* **1981**, *9*, 235.
2. Gololobov, Y. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437.
3. For a recent, general review of nonmetal azide chemistry, see: Bertrand, G.; Majoral, J.; Baceiredo, A. *Acc. Chem. Res.* **1986**, *19*, 17.
4. (a) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1977**, *16*, 2519. (b) Wilburn, J. C.; Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 1429.
5. (a) Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1969. (b) Niecke, E.; Schoeller, W. W.; Wildbredt, D.-A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 131.
6. (a) Niecke, E.; Flick, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 134. (b) Scherer, O. J.; Kuhn, N. *Chem. Ber.* **1974**, *107*, 2123.
7. Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541; and references cited therein.
8. Shaw, Y. S.; DuBois, D. A.; Neilson, R. H. *ACS Symposium Series* **1988**, *360*, 385.
9. Shaw, Y. S.; DuBois, D. A.; Watson, W. H.; Neilson, R. H. *Inorg. Chem.* **1988**, *27*, 974.
10. Li, B.-L.; Neilson, R. H. *Inorg. Chem.* **1986**, *25*, 361.

11. For related work on B-N-P compounds, see, for example: (a) van Bonn, K.-H.; Schreyer, P.; Paetzold, P.; Boese, R. *Chem. Ber.* **1988**, *121*, 1045. (b) Paetzold, P.; von Plotho, C.; Niecke, E.; Rüger, R. W. *Chem. Ber.* **1983**, *116*, 1678. (c) Maringgele, W.; Meller, A.; Nöth, H.; Schroen, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33*, 673. (d) Nöth, H.; Storch, W. *Chem. Ber.* **1977**, *110*, 2607. (e) Niecke, E.; Bitter, W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 56.
12. Fluck, E.; Heckmann, G. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L. D., Eds.; *Methods in Stereochemical Analysis*; VCH Publishers; Deerfield Beach, Florida, 1987; Vol. 8, Chapter 2.
13. Maler, L. *Helv. Chim. Acta* **1963**, *46*, 2667.
14. Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1982**, *21*, 3568.
15. Scherer, O. J.; Kuhn, N. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 811.

Table I. NMR Spectroscopic Data^{a,b}

Compound		¹ H NMR		¹³ C NMR		³¹ P NMR
(R = Me ₃ Si)	Signal	δ	J _{PH}	δ	J _{PC}	δ
$ \begin{array}{c} \text{Me} \quad \text{tBu} \\ \quad / \\ \text{R}_2\text{N}-\text{P}=\text{N}-\text{B} \\ \quad \backslash \\ \text{Ph} \quad \text{NR}_2 \end{array} $ <p>2</p>	R ₂ NB	0.08		4.75		0.7
	R ₂ NP	0.24		5.69		
	tBu	0.90		30.77		
	PMe	1.79	13.1	23.69	77.8	
	Ph	7.3-7.7 ^c	C ¹	141.79	122.2	
			C ^{2,6}	131.12	11.2	
			C ^{3,5}	128.12	13.0	
			C ⁴	130.44	2.9	
$ \begin{array}{c} \text{Me} \quad \text{tBu} \\ \quad / \\ \text{R}_2\text{N}-\text{P}=\text{N}-\text{B} \\ \quad \backslash \\ \text{Me} \quad \text{NR}_2 \end{array} $ <p>3</p>	R ₂ NB	0.10		4.90		8.9
	R ₂ NP	0.33		6.03	1.8	
	tBu	0.86		30.75		
	PMe ₂	1.62	12.9	24.35	79.2	
$ \begin{array}{c} \text{Ph} \quad \text{tBu} \\ \quad / \\ \text{Me}_2\text{N}-\text{P}=\text{N}-\text{B} \\ \quad \backslash \\ \text{Me}_2\text{N} \quad \text{NR}_2 \end{array} $ <p>4</p>	R ₂ NB	0.15		4.03		3.6
	tBu	0.91		30.34		
	Me ₂ N	2.59	11.2	37.16	3.9	
	Ph	7.4-7.6 ^c		127-142 ^c		
$ \begin{array}{c} \text{CHR} \\ // \\ \text{R}_2\text{N}-\text{P} \\ \backslash \\ \text{N}-\text{B} \\ \quad \backslash \\ \quad \text{tBu} \\ \quad \quad \backslash \\ \quad \quad \text{NR}_2 \end{array} $ <p>5</p>	R ₂ NB	0.25		4.34		56.3
	R ₂ NP	0.12		2.92	5.4	
	CHR	0.05		1.60	4.1	
	tBu	0.86		29.92		
	CHR	1.00	13.0	27.30	78.4	

Table I. Continued

Compound (R = Me ₃ Si)	Signal	¹ H NMR		¹³ C NMR		³¹ P NMR
		δ	J _{PH}	δ	J _{PC}	δ
	R ₂ NB	0.28		4.36		3.6
	R ₂ NP	0.12		3.47	2.9	
	NR	0.33		7.15	1.8	
	t _{Bu}	1.03		29.23		

^aChemical shifts relative to Me₄Si for ¹H and ¹³C spectra and to H₃PO₄ for ³¹P spectra; coupling constants in Hz. Solvents: CDCl₃ or CH₂Cl₂. ^bThe ¹¹B NMR spectra of compounds 2-6 all consist of broad singlets in the range of δ 40-43 (i.e., downfield relative to BF₃•OEt₂). ^cComplex multiplet.

Table II. Preparative and Analytical Data

Compound	Yield	bp	Analyses ^a	
	%	^o C/mm Hg	%C	%H
2	70	(117-120) ^b	52.81 (52.57)	10.02 (10.10)
3	25	120-124/0.03	47.17 (46.65)	10.98 (11.02)
4	71	140-147/0.1 (64-65) ^b	54.53 (54.79)	9.94 (10.05)
5	68	122-125/0.01	46.14 (46.24)	10.56 (10.60)
6	72	(133-136, d) ^b	43.62 (43.85)	10.29 (10.38)

^aCalculated values in parentheses. ^bMelting points in parentheses.